

Time-resolved Studies of Phase Transition Dynamics in Strongly Correlated Manganites

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Abstract. Ultrafast light pulses can be used to control electronic, magnetic and structural phases of complex solids. Here, we investigate the dynamics of insulator-metal phase transitions in colossal magnetoresistive (CMR) manganites by a combination of femtosecond visible-to-midinfrared pump-probe techniques and transport measurements. We show that an insulator-metal transition can be stimulated in CMR manganites by both above bandgap excitation and selective excitation of individual vibrational degrees of freedom. These two approaches rely on the ultrafast manipulation of parameters controlling the electronic filling and the electronic bandwidth respectively, extending the concepts of filling and bandwidth control to the ultrafast timescale. The ultrafast vibrational control of correlated-electron phases may provide new insights into the role played by lattice vibrations in determining the electronic properties of complex solids.

1. Introduction

Manganites pose an important and convenient testing ground for studying electron correlation phenomena and exhibit close analogies with a wide variety of materials in the correlated-electron family, including high- T_c superconducting cuprates [1]. In these systems, the strong interplay between charge, spin, orbital and lattice degrees of freedom results in rich phase diagrams. Phase competition at the boundaries between these phases leads to a number of remarkable phenomena including charge-ordered and striped phases, orbital and magnetic ordering, half-metallicity, phase separation, and colossal magnetoresistance (CMR) [2]. Arguably, the most striking aspect of the physics of manganites is the occurrence of a number of metal-insulator transitions, initiated for instance via perturbations of temperature, magnetic field, pressure, and irradiation with light.

To date the various electronic phases, structural phases, and correlation phenomena in manganites have been studied primarily in the quasi-static regime, as a function of *adiabatic* changes in doping, pressure, temperature, and applied field. Within the Hubbard model [3], an insulator-metal transition in a solid can be controlled by acting on two parameters: the electronic bandwidth and the electronic

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filling. In an $A_{1-x}A_xBO_3$ perovskite, the amount of doping divalent ions, x , controls the electronic filling, which can promote the delocalization of the charge via the double-exchange mechanism [3]. On the other hand, bandwidth control relies on the dependence of the transfer energy on the lattice distortion [3]: the smaller the ionic radii of cations at the A site of the perovskite lattice, the smaller the transfer integral and the larger the tendency to charge localization. Here, we demonstrate two analogous routes for the ultrafast control of insulator-metal transitions in correlated solids. In a photoinduced phase transition, the sudden electronic rearrangements due to photocarrier generation are shown to melt the charge and orbitally ordered state, driving the solid into a metastable metallic phase. In a vibrationally induced phase transition, midinfrared pulses are used to trigger selective structural modulations that modulate the electronic bandwidth [4].

2. Photo-induced phase transition in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$

$\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (PCMO) is a unique example among manganites, exhibiting insulating behavior over the entire chemical composition (x) and temperature range [5]. This is a consequence of the small ionic radius of Ca, which results in a pronounced orthorhombic distortion (Figure 1a) that favors charge localization. Notably, the insulating phase at $x=0.3$ adjoins a “hidden” metallic state of the system, characterized by enormous changes in resistivity. A 10-order-of-magnitude “colossal” negative magneto resistance is found at low temperatures at this doping level, associated with melting of the charge- and orbital-ordered state [5]. Other external stimuli can trigger insulator-metal transitions with comparable conductivity changes. Photo-excitation, application of static electric fields and pressure, x-ray irradiation and electron irradiation have been found to melt the charge-ordered, insulating state [2].

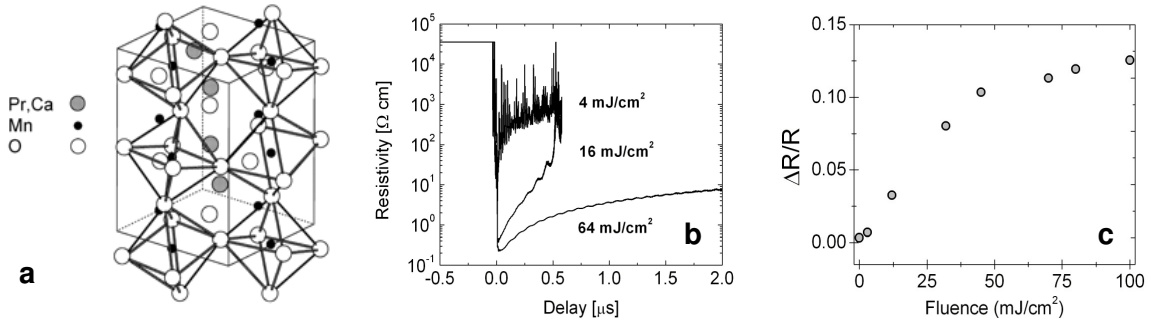


Figure 1. (a) Perovskite crystal structure of PCMO with pronounced orthorhombic distortion. (b) Time-resolved resistivity measurements following photoexcitation at 800 nm for 4, 16 and 64 mJ/cm^2 pump fluence. (c) Fluence dependence of photoinduced reflectivity changes at 800 nm measured 300 fs after photoexcitation at the same wavelength.

Time-resolved resistivity measurements in photo-excited PCMO at 77 K were performed first, evidencing a photo-induced transition to the metallic state (Figure 1b). A current amplifier was placed in series of the sample, which was held between two gold electrodes deposited on the surface. A prompt resistivity drop was observed from the static value of $3 \cdot 10^4$ [$\Omega \text{ cm}$] to approximately 100 [$\text{m}\Omega \text{ cm}$]. This conductivity change is of similar magnitude as that obtained by application of a 6T magnetic field at this temperature and doping [5]. The formation of the metallic state results in characteristic modifications of the reflectivity spectrum of PCMO at eV energy scales [6], deriving from melting of the charge order, collapse of the 0.3 eV insulating gap and formation of a pseudo plasma edge in the metallic state. Femtosecond pump-probe experiments were used to probe the time-dependent reflectivity of PCMO following photoexcitation. Figure 1c shows reflectivity changes at 800 nm measured 300 fs after excitation as a function of pump fluence. The fluence dependence of such changes exhibits highly non-linear behavior, with a threshold near 1 mJ/cm^2 , non-linear growth and

saturation above 40 mJ/cm² (Figure 1c). This behavior and the long lifetime of the high conductivity state are indicative of cooperativity in the de-stabilization of charge-order and in a phase transition.

3. Phono-induced phase transition in Pr_{1-x}Ca_xMnO₃

Coherent THz excitation of specific infrared-active modes can control the electronic phase of a manganite via direct modulation of structural parameters which determine the electronic bandwidth of these systems. In ABO₃ perovskites, the orthorhombic distortion is quantified by the geometric “tolerance factor” that depends on the average A-O (A=Pr,Ca) and B-O (B=Mn) distances:

$$\Gamma = \frac{(A - O)}{\sqrt{2}(Mn - O)}$$

$\Gamma = 1$ corresponds to a cubic structure, while $\Gamma < 1$ reflects a compression of the Mn-O bond and an elongation of the A-O bond. Γ is related to the electronic properties of the solid via the one electron bandwidth (W), since the capacity for $3d$ -electrons to hop between neighboring Mn-sites depends on super-transfer process via O($2p$) states and on the degree of overlap between orbitals in neighboring sites [2-3]. The hopping matrix element is maximum at $\theta = 180^\circ$ (cubic), and decreases with θ , vanishing at $\theta = 90$. Figure 2a shows the low-temperature optical conductivity spectrum of PCMO with three prominent phonon modes (23, 42, and 71 meV) [7]. The two highest frequency vibrations are assigned to the Mn-O-Mn bending mode and the Mn-O stretching mode respectively. Both vibrational modes modulate the geometrical parameters determining the tolerance factor and are thus expected to have a strong coupling to the electronic properties of the system. Here we study the effect of large-amplitude excitation of the highest-frequency Mn-O stretching vibration at 17 μm (17 THz or 580 cm⁻¹) by means of intense femtosecond mid-infrared pulses. The material response is investigated using both ultrafast pump-probe spectroscopy and transient conductivity.

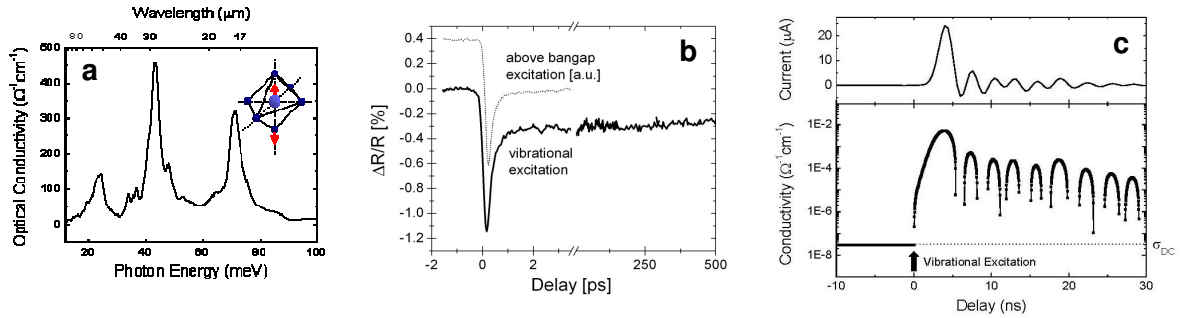


Figure 2. (a) Low temperature optical conductivity spectrum of PCMO. The inset shows the atomic displacements within the MnO₆ octahedra associated with the 17- μm phonon. (b) Relative change of reflectivity at 800 nm ($\Delta R/R$) as a function of pulse delay following vibrational excitation at 17 μm (solid line) and 800-nm photo-excitation (dotted line). (c) Time-dependent transport measurements, showing that vibrational excitation results in a $\sim 10^3$ increase in the sample current (upper panel) and a $\sim 10^5$ increase in the sample conductivity (lower panel). The experimental setup is the same as in the photoconductivity measurements described in Section 2.

In the pump-probe spectroscopy studies, PCMO samples at 30 K are excited by 200 fs laser pulses centered at 17 μm , and the transient changes in reflectivity are measured over a broad spectral range (visible to near-infrared) in order to identify the characteristic spectral signatures and formation time of the metallic phase. Figure 2b shows the transient reflectivity ($\Delta R/R$) at 800 nm following impulsive vibrational excitation (at a fluence of $\sim 1\text{mJ/cm}^2$) and compared with above-bandgap pulsed excitation. The reflectivity responses are identical, with large long-lived changes in reflectivity

developing within 1 ps of excitation. These changes are only observed for resonant excitation of the 17 μm phonon and exhibit threshold and saturation dependence on the pump fluence, characteristic of a phase transformation to the metallic state, as previously established for *above-bandgap* excitation (see Section 2). The spectrum of the reflectivity changes exhibits identical features as in the photoinduced case, with decreased reflectivity at photon energies in the 0.5-1.9 eV range and increased reflectivity at higher photon energies. These measurements provide evidence that the metallic state is formed promptly (within the 200 fs experimental resolution) via direct vibrational excitation, and that this state persists for 100's of picoseconds.

Changes in the sample conductivity are monitored by measuring the transient sample resistance following mid-IR excitation, in the same experimental configuration as described in the previous Section. Mid-infrared excitation results in a 1000-fold increase in current (Figure 2c, upper panel). The high conductivity state develops and relaxes within the 4-ns resolution of the electronics. Figure 2c (lower panel) shows the 10^5 increase of the sample conductivity derived from the measured transient resistance by assuming that the transition to the conductive state is uniform throughout the excited sample volume. In these measurements, contributions from multiphoton interband carrier excitations are negligible (five photons at 17 μm are required to span the 0.3-eV insulating-bandgap of PCMO) and the moderate temperature jump due to laser excitation (estimated at <2 K) can be ruled out as the origin of the resistivity drop. These results clearly show that resonant excitation of the Mn-O phonon vibration in PCMO drives the system, in the *electronic ground state*, into a metastable, nanosecond-lived, high-conductivity phase.

The excitation of a specific phonon mode can thus trigger a transition toward a competing phase of the system. The ultrafast vibrational control of correlated-electron phases is likely applicable in other complex solids, providing new ways of studying electron correlation effects and the coupling between crystal structure and the conduction properties of strongly correlated electrons.

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